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Preliminary communication

Narrowing of spontaneous emission and lasing in lyotropic and thermotropic liquid crystals

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The narrowing of spontaneous emission and lasing are reported for the first time for a dye-doped lyotropic liquid crystal consisting of a methylbenzylamine solution of polybenzylglutamate (PBLG). Lasing was also studied in twisted nematics based on cholesterol derivatives. PBLG produces a cholesteric liquid crystal (CLC) with selective reflection in the visible region at PBLG concentrations above 55%. A comparison is made of the narrowing of spontaneous emission and lasing in lyotropic *vs*. thermotropic liquid crystals. In both cases lasing occurs where the selective reflection band overlaps the dye emission band. Thermotropic liquid crystals show a much lower lasing threshold than lyotropic systems. The lasing mechanism and the role of disorder in both systems are discussed.

Lasing from dye-doped cholesteric liquid crystals, CLCs, used as active optical resonators has recently become a subject of intense study [1–5]. CLC lasing studies started in the 1970s when optically pumped lasing in dye-doped CLCs was first observed [6]; later experiments were carried out by Ilchishin *et al*. [7, 8]. These early papers discussed lasing in terms of distributed feedback theory, arguing that the light emitted by the dye within the selective reflection band would experience multiple reflections and a considerable delay before emerging from the material; lasing in thermotropic CLCs far off the middle of the reflection band was attributed to band-shifting effects of helical structure distortions.

A planar monodomain CLC is a one-dimensional photonic band gap (PBG) structure with a selective reflection band for light circularly polarized in the same sense as the cholesteric helix. CLC properties are similar to those of other one-dimensional PBG materials: both the stimulated emission and lasing of circularly polarized light from the planar texture [1, 2, 5] of ideal cholesteric liquid crystalline monodomain structures are reduced in the middle of the reflection band, since, for circularly polarized light, the emission is proportional to the density of states, which is zero within the reflection band. In band-edge modes, however, the photon dwell time is longer and this provides much better conditions for lasing. The effect of the longer photon dwell time is most conspicuous in monodomain samples where the cholesteric helix is the least distorted and the PBG structure is almost ideal.

In the mid-band gap, lasing becomes possible in the samples where a disorder or multidomain structure causes new modes to appear and may result in low threshold 'random lasing' reported in a number of systems, including solutions of colloidal microparticles [9]. The concept of random lasing, first introduced by Letokhov [10], suggests that repeated scattering makes photons linger in the medium. However, the effect of disorder on lasing properties of cholesteric materials has not yet been studied.

Domain structure and director fluctuations in PBLG-based CLCs should help random lasing. On the other hand, lasing is suppressed by the extremely poor birefringence of cholesteric layers in PBLG solutions and in many other lyotropic systems. Understanding in which materials certain types of lasing would prevail is an important step towards solving the problem of low threshold lasing in cholesteric materials. The purpose of this work is to study lasing in a dye-doped cholesteric

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PBLG solution as a model of lasing from lyotropic CLCs, and to compare lasing in lyotropic *vs.* thermotropic cholesteric materials. PBLG is a low birefringent material and one of the few polypeptides that are relatively easy to synthesize in a laboratory. A PBLG solution has not yet been studied as a matrix for lasing dyes. We report here our first observations of the narrowing of spontaneous emission and lasing in concentrated dye-doped methylbenzylamine/toluene solutions of PBLG and in thermotropic CLCs based on cholesterol derivatives.

PBLG (figure 1; Polysciences, Inc.) was used as received and had molecular mass of 100 000 to 150 000. Methylbenzylamine, both racemic and non-racemic, was obtained from Aldrich Chemical Co. The CLCs were doped with pyrromethane 597 (Exciton), a laser dye whose emission band lies within the selective reflection band, and absorption and emission peaks in toluene are 526 and 575 nm, respectively. Pyrromethane 597 is highly miscible with the CLC; however, to avoid aggregation of dye molecules, only low dye concentrations (about 0.6%) were used. A mixture of nematic ZLI 4788 (Merck Co.) and cholesterol derivatives was used as a thermotropic CLC. Chiral dopants, viz. cholesteryl pelargonate and cholesteryl oleate (Aldrich Chemical) were used as received. The chiral nematic was 17 wt% cholesteryl oleate, 32 wt% cholesteryl pelargonate, and 51 wt% ZLI 4788.

PBLG solutions in toluene, dichlorethane and methylbenzylamine were studied. Known amounts of PBLG and methylbenzylamine were dissolved in excess dichlorethane and/or toluene with subsequent weight-controlled toluene evaporation. The viscous solution of PBLG or of the thermotropic cholesteric was placed and sealed between two rubbed polyimide-coated glasses. Cell thickness varied from 10 to 150 μm.

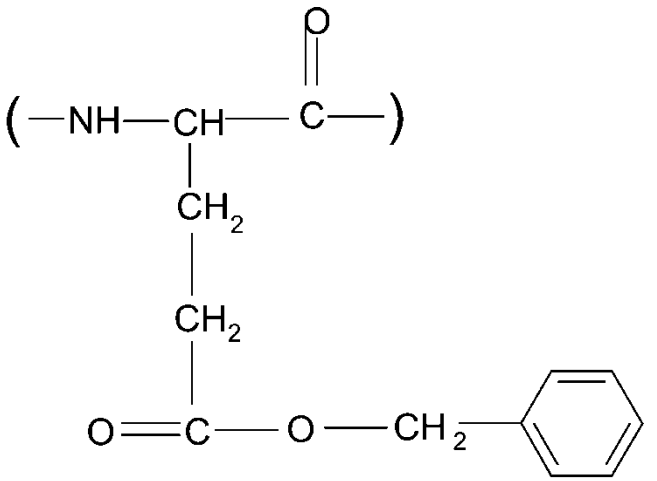

Figure 1. PBLG molecule.

After 30 days of cell exposure at ambient temperatures, sample morphology was checked. A Nd:YAG beam was used to excite the dye near its absorption maximum and the emission was focused on the monochromator entrance slit. The pumping beam diameter was *c.* 60 μm.

Concentrated PBLG solutions produce structures with iridescent colour at methylbenzylamine concentrations of 55 to 65%. Iridescence suggests cholesteric structure, but the selective reflection band was distinct only in some areas of the samples (figure 2). Selective reflection is adversely affected by irregular morphology and intense light scattering. The samples show iridescence associated with shifting the selective reflection band. The absence of fine structure at the edge of the selective reflection band even in thin cells suggests multidomain structure of the PBLG samples. Poor birefringence of cholesteric layers makes the selective reflection band narrow, typically 20–25 nm. In fact the selective reflection band of a monodomain should be narrower since the transmission spectrum reflects some broadening due to contribution from several domains. In contrast, thermotropic liquid crystals show a much broader selective reflection band with fine edge structure in 10 to 12 μm thick cells (figure 3), but as thickness increases, this structure fades to vanish completely at 40 μm.

A cholesteric medium may be considered to consist of numerous thin birefringent planar sections with ordinary and extraordinary refractive indices n_o and n_e

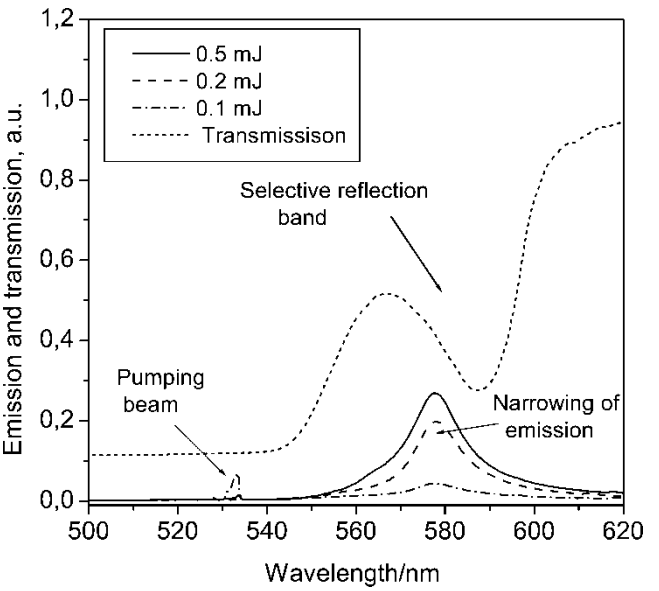

Figure 2. Narrowing of spontaneous emission from a concentrated methylbenzylamine solution of PBLG, the position of the selective reflection band of a thicker sample is shown.

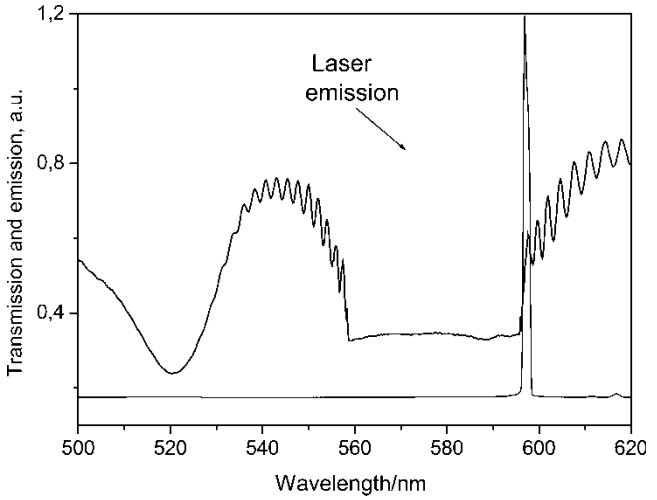

Figure 3. Lasing from a thermotropic CLC based on cholesterol derivatives.

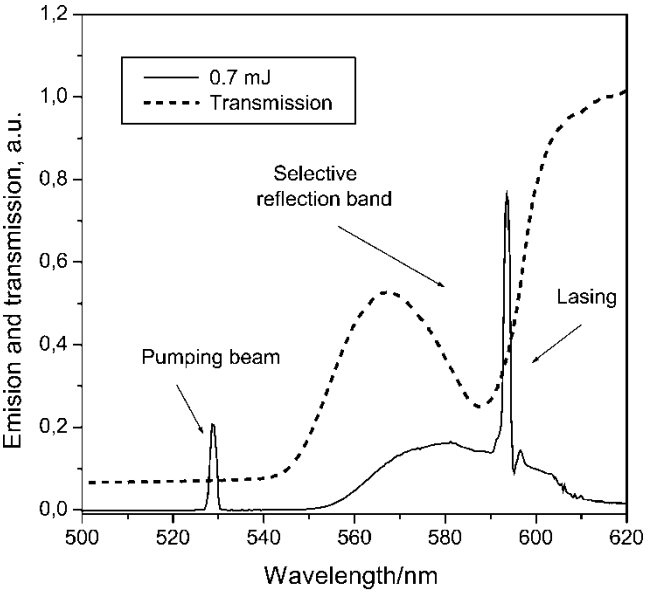

Figure 4. Lasing from a concentrated methylbenzylamine solution of PBLG, with typical selective reflection.

in the plane. The mid-wavelength of the selective reflection band is:

$$\lambda_c = P\left(\frac{n_o + n_e}{2}\right) \quad (1)$$

where P is the pitch of the cholesteric helix. The width of the selective reflection band is proportional to the birefringence $\Delta n = n_e - n_o$,

$$\Delta\lambda = P(n_e - n_o). \quad (2)$$

The indices calculated based on equations (1) and (2) were: for PBLG, $n_o = 1.518$ and $n_e = 1.543$; and for the thermotropic sample, 1.4535 and 1.6185, respectively. In the case of PBLG the broadening of the selective reflection band results in a greater calculated Δn than the observed birefringences. In PBLG, a narrowing of the spontaneous emission occurs at pumping energies of 0.1 to 0.5 mJ, being most noticeable where the spontaneous emission peak overlaps the selective reflection band (figure 2).

Lasing can be seen only in those domains having good planar structure. Figure 4 shows a typical lasing peak. The lasing line may be narrow, about 1–3 nm, and may also consist of several narrow peaks. No lasing is observed where the selective reflection band is significantly shifted (by >40 nm) from the dye emission peak. Different sample areas show lasing at both edges of the selective reflection band. In thermotropic liquid crystals lasing occurs at the long wavelength edge of the selective reflection band, even at much lower pump energies, but shifting the selective reflection band slightly towards longer wavelengths by reducing the chiral dopant concentration causes lasing at the short wavelength edge of the selective reflection band.

The estimated lasing threshold in 40 μm thick PBLG samples is about 18×10^4 W mm^{-2}. In thinner samples, only the narrowing of spontaneous emission is detectable. In 40 μm thick thermotropic liquid crystal film with nearly perfect planar texture, the lasing threshold is about $(1\text{–}2) \times 10^4$ W mm^{-2}, then grows as the thickness significantly decreases, and at 8 μm only the narrowing of spontaneous emission can be seen. Thus, in 40 μm thermotropic samples the lasing threshold is an order of magnitude lower than in PBLG sample of the same thickness. Moreover, lasing thresholds in PBLG are higher than those recently found in lyotropic polyisocyanates [5]—apparently due to greater disorder in PBLG-based CLCs with their multidomain structure with randomly oriented small domains and lower birefringence of nematic layers.

Domain size has a major effect on lasing thresholds in band edge modes; the lowest thresholds can be expected in large and uniform domains. In 40 μm thick lyotropic and thermotropic samples, band edge lasing could not be attributed to a specific mode, since multidomain structure suppresses the oscillations at the band edge. The main factor raising the lasing threshold at the selective reflection band edge is the cholesteric structure irregularity caused by director fluctuations, sample defects and multidomain structure, all resulting in the broader band edge modes. Broader modes reduce photon lifetimes and the quality factor of cholesteric resonator ('Q factor') for the mode as given by

$$Q \approx \lambda/\Delta\lambda \quad (3)$$

where λ is the mode wavelength and $\Delta\lambda$ is the mode width. The mode width $\Delta\lambda$ becomes smaller with

increasing birefringence of cholesteric layers $\Delta n = n_e - n_o$. The Q factor is proportional to the photon dwell time, $\tau = Q/2\pi\nu_c$: the higher τ is, the lower the lasing threshold, so lower Q factors will result in higher lasing thresholds.

In spite of the multidomain structure, no random lasing (numerous lasing peaks on the top of the emission band) was observed in PBLG, apparently because of the low optical birefringence of cholesteric layers and, accordingly, low interdomain variation of the refractive index. Such conditions produce no light waveguide loops essential for random lasing. Work is underway to study physical characteristics of defects and their role in boosting spatially localized states, to solve the problem of lasing beam coherence, and to study coherence length effects on domain properties of the liquid crystal.

In summary, light emission from dye-doped CLCs with a visible region selective reflection band overlapping the dye emission band was studied in lyotropic and thermotropic systems. In lyotropic liquid crystals lasing occurs only in thicker samples, with lasing thresholds an order of magnitude higher than in thermotropic samples. Lasing from a lyotropic CLC is explained in terms of a PBG structure of disoriented cholesteric domains rather than in terms of random lasing caused by non-uniformity of the refractive index. The higher lasing thresholds of PBLGs are a result of a much less regular planar cholesteric structure and lower birefringencies than those in lyotropic polyisocyanates. The more regular planar cholesteric structure of thermotropic samples gives lower lasing thresholds. However, the lyotropic PBLG can be potentially used as a lasing material in the new photonics-based generation of biosensors and chips.

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